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Aligned electrospun nanofiber poly(lactic acid) mats coated with conductive polyaniline: Anisotropy of electrical conductivity

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ABSTRACT

Conductive mats of polylactic acid/polyaniline PLLA/PANI aligned nanofibers are prepared starting from aligned nanofiber mats of PLLA. The average DC-conductivity of the composite mats is 0.18 ± 0.02 S. cm^{-1} in the parallel direction of fibers and 0.03 ± 0.004 S. cm^{-1} in the perpendicular direction. In comparison with published DC-conductivity values of PANI nanofiber composite or blend mats with PLLA or with other polymers, the current mats exhibit good DC-conductivity values and better anisotropy of electrical conductivity. The study of aging effect on the DC-conductivity reveals an exponential decrease with a characteristic time of $\tau \approx 9$ weeks. The electrical impedance spectroscopy shows an ohmic and capacitive behavior of the composite mat.

1. Introduction

Electrospinning is a well-established technique for fabricating nanofiber nonwoven mats from natural or artificial polymer solutions [1]. The large number of controllable parameters of this technique, namely those concerning the polymer solution (type of solvents, polymer concentration, viscosity, surface tension, conductivity, …) and those related to the spinning process (engaged DC voltage, flow rate of polymer solution, distance between the nozzle and the collector, nozzle diameter, ambient temperature, air humidity …) facilitates the creation of fibrous nanostructured mats with customized characteristics, including fiber diameters, porosity and alignement [2]. However, the diversity of those parameters renders the optimization process a challenging task [3].

The growing interest in nanostructured conducting polymers using the electrospinning technique is credited to their expanding applications [4,5]. Those nanostructured mats have many novel electronic applications such as; solar cells [6,7], energy harvesting [8,9], tissue engineering [10,11], sensing devices [12,13], actuators [14,15], light emitting diodes [16], filtration membranes [17] and electromagnetic interference shielding [18,19]. Among conductive polymers, polyaniline (PANI) is one of the most widely investigated, owing to its easy synthesis, environmental stability and excellent electrical conductivity that can be tuned by the oxidation and protonation states [3]. However, the solubility of PANI in most organic solvents is unsatisfactory, making it difficult to fabricate uniform structures of electrospun nanofibers using PANI solely [20,21]. Therefore, two approaches have been proposed to prepare conductive nanofibrous mats using this remarkable polymer. The first one consists of coating a non-conducting nanofiber substrate with polyaniline using bulk oxidative solution polymerization process [22,23], and the second approach relies on electospinning PANI blends with more flexible, high molecular weight polymers that act as processing aids [7,20,24].

In a previous work of the authors, random PLLA/PANI composite nanofiber mats were prepared by bulk oxidative solution polymerization of aniline hydrochloride onto random electrospun PLLA nanofibers [23]. Herein, we present a new kind of aligned PLLA/PANI composite nanofiber mats prepared by polymerizing aniline hydrochloride onto aligned electrospun PLLA nanofibers. To the best of authors' knowledge, this kind of aligned PLLA/PANI composite nanofiber mats with high DC-electrical conductivity has not been prepared before. The DC-conductivity of the aligned nanofiber mats and its temporal decay are investigated. The anisotropy of the DC-conductivity is also discussed. The present study also aims at optimizing the polymerization parameters in order to achieve good adherence of PANI onto PLLA. This would significantly increase the conductivity of the nanofiber mats with superior mechanical properties endowed by the supporting PLLA nanofibers. The impedance spectroscopy of the mats is also studied and the elements of the equivalent electrical circuit are determined. The alignment of PLLA fibers, their successful coating with PANI and the regularity and thickness of the deposited layer are assessed by Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM). The structural characterization of the mats by FTIR and UV–vis spectroscopies are independent of fiber alignment and they are discussed in the

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above-mentioned previous work of the authors [23].

2. Experimental

2.1. Reagents and chemicals

Polylactic acid (PLLA, M_w = 150 000 g/mol) was obtained from Nature-Works. Anilinium chloride monomer, tetra n-butyl ammonium bromide (TBAB), ammonium peroxydisulfate ($(NH_4)_2S_2O_8$, APS), dichloromethane, acetone and hydrochloric acid are from Merck. All chemicals are of analytical grade and are used without further purification.

2.2. Preparation of aligned electrospun PLLA nanofiber mats

The procedure of the preparation of spinnable solution and the optimization of the electrospinning parameters have been published in a previous work of our team [23]. In short, the concentration of the spinnable solution is 6 wt% in dichloromethane. The inner and outer diameter of the needle is 0.6 and 0.8 mm, respectively. The flow of the spinnable solution was performed using a programmable syringe pump (TOP-5300), whereas the high-voltage power supply was an ES813-D50.1 Dual output: 0–± 50kV/1 mA Electrostatic/HV Generator (USA).

In order to prepare aligned fibers, the collector was a stainless steel drum having 10 cm diameter, 25 cm length and 1 mm thickness, covered with an aluminum foil.

The feed rate of the solution was set at 1 $ml.h^{-1}$ and the distance between the collector and the needle tip was fixed at 10 cm.

The voltage was kept in the range 18–20 kV during the experiments. The drum's rotation speed was 3500 rpm. The experimental temperature inside the electrospinnig chamber was 22 ± 2 °C, and the relative humidity was maintained between 40 and 50% to have a good evaporation of the solvent. The duration of the electrospinnig process was 3 h, [Fig. 1(a)].

Then, the mats were left on the drum inside the electrospinning chamber for 2 h at the room temperature to complete the volatilization of dichloromethane, [Fig. 1(b)]. Then, aluminum foil was pulled up from the drum and divided into six equal pieces (12.5 × 10.5 cm). Then, the mats were peeled off from the aluminum foils and kept in the dark in a closed vessel.

2.3. Preparation of aligned PLLA/PANI composite nanofiber mats

Aligned PLLA/PANI composite nanofiber mats was produced using the free radical oxidative solution polymerization process. The procedure of the preparation is identical to that used for the preparation random PLLA/PANI composite nanofiber mats, and it was published previously [23]. Details about the optimization of polymerization process are included in the **Supplementary Information Document**. Briefly, PLLA aligned nanofibers mat was immersed into aniline hydrochloride solution (10 mmol in 25 mL of deionized water) under the ultrasonic stirring for 30 min. When the mat is saturated with aniline solution the APS solution (12.5 mmol in 25 mL of deionized water) is then added dropwise to the above mat for further 30 min. The mat was left for 5 h to complete the polymerization. Next, the mat was washed repeatedly with deionized water and acetone until the acetone washings were colorless. Then, it was washed three times with 50 mL of 0.2 M HCl, and similarly with acetone. Finally, the mat was dried in a desiccator at 40 °C and stored in the dark in a closed vessel.

2.4. Characterization

2.4.1. PLLA and PLLA/PANI mats morphology

The mat morphology is performed using Tescan Vega-II XMU5136 variable pressure scanning electron microscopy (SEM), and Zeiss-EM10C-100 kV transmission electron microscopy (TEM). Mats are coated with graphite to promote the contrast of the SEM micrographs using EMITECH K975 carbon evaporator. Mat thickness is measured using a digital micrometer (Mitutoyo CLM1). The nanofiber diameters are measured using Image-J software.

2.4.2. Electrical measurements

DC conductivity (σ) measurements are performed on newly prepared samples (12 mats), using a four-probe homemade device consisting of four parallel contacts positioned 2 mm away from each other. Each contact is made of five adjacent platinum wires of 0.1 mm diameter. The contact length of each probe is 3 cm [Fig. 2(a)]. KEITHELY-220 is used as a programmable Current Source and KEITHELY-617 is used as a programmable electrometer. 20 kPa pressure is applied on the upper surface of the mat to achieve a good contact between the mat and the electrodes. σ is calculated using Van der Pauw's relation $\sigma = \frac{d}{t \times w}\frac{I}{V}$. Where d is the distance between the electrodes (cm), t and w are the sample thickness and width respectively (cm).

For each aligned PLLA/PANI composite mat, 20 measurements are carried out (10 measurements on each side); five measurements are in the parallel direction of the fibers and the other five are in the perpendicular one.

The temporal decay of the DC-conductivity of the as-prepared composite nanofiber mats is evaluted by measuring their conductivity (σ) during 20 weeks (one measurement per week). In this study, the conductivity values according to the parallel direction of the fibers are only considered as they are more important, and they are more characteristic of this type of mats.

The mats were stored in closed vessels in the dark to keep them away from any possible influence of humidity and light. The DC-conductivity of each mat was periodically measured with the four-probe device. Then, it was re-desiccated to eliminate any traces of humidity and stored again. Measurements were conducted at room temperature

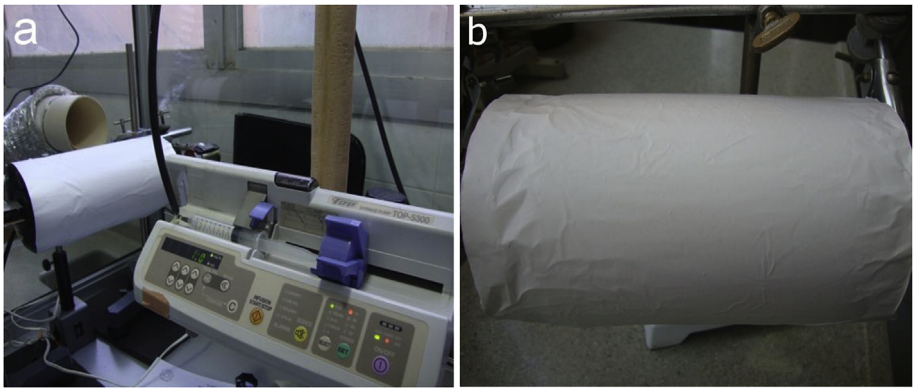

Fig. 1. Photos of: (a) the electrospinning chamber, (b) aligned PLLA nanofiber scaffold on drum.